

Chapter 2

Methodology

In this chapter, the raw materials, the preparation of specimens, the testing methods and the equipments used in this research are introduced in detail. On the basis of the following measurements, the obtained experimental data are discussed in the following chapters.

2.1 Raw Materials

2.1.1 *Cement*

Three batches of commercial cement were employed in this research, respectively corresponding to Cement I, Cement II and Cement III. Cement I and II were provided by China Building Materials Academy and Cement III was from Lafarge Shui On Cement Co. Ltd. All the three batches of cement comply with the Chinese standard GB8076-2008, whose chemical and mineralogical compositions are listed in Table 2.1.

2.1.2 *Superplasticizers*

Two types of superplasticizers were used in this research including a self-synthesized polycarboxylate (PCE) type superplasticizer and a commercial polycondensate type superplasticizer of β -naphthalene sulfonate formaldehyde (NSF). Their molecular structures are shown in Fig. 2.1.

The PCE superplasticizer was a comb-shaped co-polymer of acrylic acid (AA), methyl polyethylene glycol methacrylate (MPEGMA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) with a monomer molar ratio of

Table 2.1 Chemical and mineral compositions of cement

Cement	Chemical composition (mass %)						Mineral composition (mass %)					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ Oeq	f-CaO	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
I	22.10	4.04	3.38	61.91	2.66	2.87	0.56	0.79	57.34	18.90	6.47	11.25
II	21.56	4.06	3.43	61.51	2.63	2.89	0.53	0.66	57.40	20.30	6.32	11.19
III	21.56	4.44	2.78	62.38	2.32	3.14	0.6	0.79	46.00	27.14	7.05	8.45

Note The composition was obtained according to EN 196-2:2005 and Chinese Standard GB/T176-2008 “chemical analysis of cement”

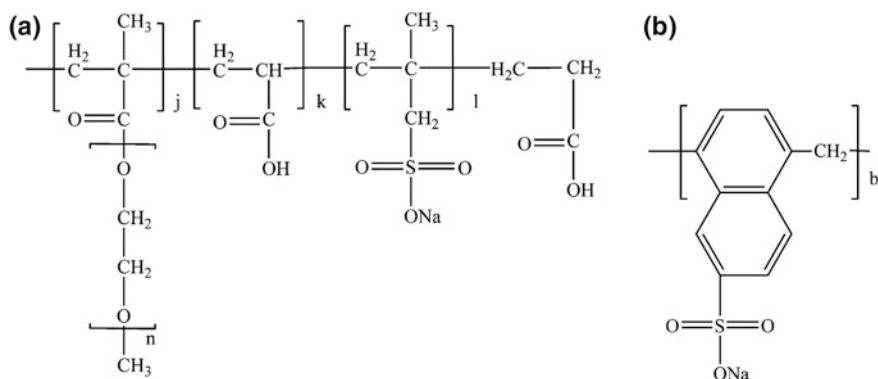


Fig. 2.1 Schematic drawing of chemical structure of superplasticizers. **a** PCE; **b** NSF

2.12:1.00:0.29 prepared via free radical polymerization by using ammonium persulfate (APS) as initiator at 80 °C. The weight average molecular weight (M_w) of MPEGMA was about 1300 and the average polymerization degree of the poly(ethylene oxide) was about 28. A general description of the preparation procedure of the PCE superplasticizer is summarized as follows. (1) 70.0 g of water was pre-charged into a flask vessel equipped with two feeding pipes. (2) The flask was firstly washed by using nitrogen gas for 3 times and heated up to 80 °C in an oil bath. (3) 196.0 g of the mixture of monomers, together with 1.3 g of the chain transfer agent, was dissolved in 170.0 g of deionized water. (4) Initiator solution was prepared by dissolving 1.0 g of APS in 40.0 g of deionized water. (5) Then the initiator solution and the monomer solution were separately fed into the vessel dropwise over 2.5 and 2.0 h respectively. (6) The inside temperature was kept constant at 80 ± 2 °C during polymerization. After completion of dosing, the whole reactant mixture was kept at 80 °C for an additional post-polymerization time of 30 min under stirring to complete the polymerization and then was allowed to cool down to a room temperature at 25 °C. An aqueous solution of PCE superplasticizer with a solid content of ca. 40 wt% was obtained. The number average molecular weight (M_n) of the synthesized PCE was 3.66×10^4 and the polydispersity index (M_w/M_n) was 2.48.

The commercial NSF superplasticizer was provided by Huadi Synthetic Material Co. Ltd.

2.1.3 Polymer Latexes

Two styrene-acrylate copolymer latexes with different particle sizes and T_g produced by BASF (China) Co. Ltd, latex L1 and latex L2, were used, whose properties are listed in Table 2.2.

Table 2.2 Properties of acrylate latexes

Polyacrylate latexes	Solid content (%)	Particle size (nm)	T _g (°C)	Viscosity (mPa.s)	pH	MFFT ^a (°C)	Density (g/cm ³)
L1	50	200	10	500–2000	7.0–9.0	12	1.03
L2	57	300	–6	140–200	7.0–8.5	<1	1.04

^aMinimum film formation temperature

Table 2.3 Properties of asphalt emulsions

Type of asphalt emulsions	Solid content (%)	Particle size (μm)	Storage stability 1 day (%)	Residue on 1.18 mm sieve (%)	Penetration depth at 25 °C (0.1 mm)	Density (g/cm ³)
Anionic	61.16	2.9	0.30	0.02	73	1.02
Cationic	59.29	3.1	0.31	0.02	98	1.02

Note These properties were measured according to Chinese Industry Standard JTJ 052-2000

2.1.4 Asphalt Emulsions

Two types of anionic and cationic asphalt emulsions were provided by China Petrochemical Corporation, whose properties are shown in Table 2.3.

2.1.5 Organic Monomers, Homo-polymers and Co-polymers

To disclose the influences of the charge feature of molecules on the adsorption and the retardation effects in cement pastes, organic monomers possessing different charges in aqueous solution, and their corresponding linear homo-polymers were chosen. Moreover, two series of comb-shaped co-polymers with varied molar ratios of functional groups in backbones were synthesized without changing the charge density.

2.1.5.1 Organic Monomers and Their Corresponding Homo-polymers

Analytical grade of chemicals, acrylic acid (AA), sodium p-styrene sulfonate (SSS), [3-(methacryloylamino) propyl] trimethyl ammonium chloride (MAPTAC) were used as received (all >98% purity). Poly(acrylic acid) (PAA) with weight average molecular weight (Mw) of ca. 5000 was provided by Beijing Chengzhi Yongchang Chemicals Co. Ltd. Analytical grade of poly(sodium-p-styrene sulfonate) (PSSS) with Mw of 70,000 was purchased from Acros Organics. Cationic polymer, poly ([3-(methacryloylamino) propyl] trimethyl ammonium chloride) (PMAPTAC) was synthesized via semi-batch radial polymerization by using ammonium persulfate

(APS) as initiator at 80 °C. 45.0 g of water was pre-charged into a flask vessel equipped with two feeding pipes. The flask was firstly washed by using nitrogen gas for 3 times and then the mixture was heated up to 80 °C in oil bath. 335.0 g of MAPTAC solution with mass concentration of 32.8% and 65.0 g of APS solution with mass concentration of 1.7% were then separately fed into the vessel dropwise in 2.5 and 3.0 h respectively. After completion of both feedings, the reactant mixture was kept at 80 °C under stirring for another 2.0 h to complete the polymerization. An aqueous solution of PMAPTAC with solid content of ca. 25.0% was obtained. The synthesized PMAPTAC sample was purified via dialysis and then analyzed by size exclusion chromatography (SEC) to measure the molecular weight distribution (described in Sects. 2.2.1 and 2.2.2).

2.1.5.2 Comb-Shaped Co-polymers

The comb-shaped co-polymers were prepared via semi-batch free radical polymerization at 80 °C by co-polymerizing the monomers of AA, MPEGMA and sodium methyl acryl sulfonate (SMAS) with monomer molar ratio of 1.0:0.47:0.13, based on the basic recipe PAS100-0, given in Table 2.4. The initiator for polymerization was ammonium persulfate (APS) and 3-mercaptopropionic acid (MPA) was used as chain transfer agent to control the molecular weight. By partly replacing the monomer AA with AMPS in the polymerization recipes, the ratio of $-\text{COO}^-$ groups to $-\text{SO}_3^-$ groups can be adjusted without changing the charge density in the synthesized polymer molecules. Thus, the effects of $-\text{COO}^-$ and $-\text{SO}_3^-$ groups in co-polymer molecules on their behaviors in cementitious system can be studied. The synthesis formula of the comb-shaped co-polymers is presented in Fig. 2.2.

Amphoteric co-polymers were synthesized based on the basic recipe PAM100-0 (Table 2.4), in which the molar ratio of monomer AA to MPEGMA was fixed at 1.0:0.25. Cationic charges can be introduced into the molecules by simply replacing the monomer AA with MAPTAC in a certain ratio and the synthesized molecules

Table 2.4 Monomer combination in synthesis of the co-polymers

No.	AA	MPEGMA1300	SMAS	AMPS	MAPTAC
PAM100-0	1	0.25	–	–	0
PAM88-12	0.88	0.25	–	–	0.12
PAM75-25	0.75	0.25	–	–	0.25
PAM50-50	0.5	0.25	–	–	0.5
PAM0-100	0	0.25	–	–	1
PAS100-0	1	0.47	0.13	0	–
PAS70-30	0.7	0.47	0.13	0.3	–
PAS50-50	0.5	0.47	0.13	0.5	–
PAS0-100	0	0.47	0.13	1	–

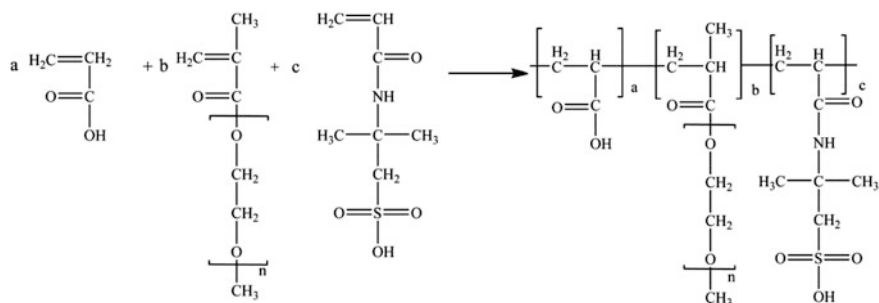


Fig. 2.2 Synthesis formula of the co-polymers containing both carboxyl and sulfonic groups

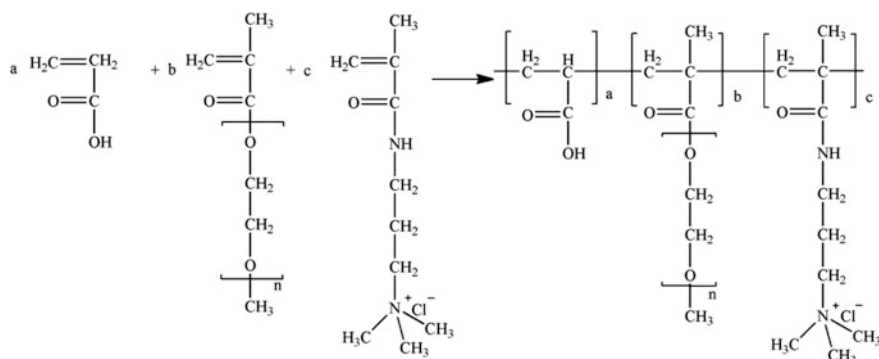


Fig. 2.3 Synthesis formula of the amphoteric co-polymers containing the cationic group $\equiv\text{N}^+$

become amphoteric. Complete replacement of AA with MAPTAC makes the produced molecule turn to cationic one (PAM0-100). The synthesis formula of the amphoteric co-polymers is presented in Fig. 2.3.

Detailed description of the preparation procedure of the above mentioned co-polymers (PAM and PAS series) is summarized as follows. Monomers with mix proportion as described in Table 2.4, together with the chain transfer agent, were dissolved in deionized water and an aqueous solution with mass concentration of 55.0% was prepared. Initiator solution with mass concentration of 2.0% was prepared by dissolving APS in deionized water. In the polymerization process, 350.0 g of monomer solution was used and the molar ratio of initiator to total monomers was fixed at 1.0%. A flask vessel filled with 35.0 g of water and 35.0 g of monomer solution as pre-charge and equipped with two feeding pipes, was firstly washed by using nitrogen gas for 3 times and heated up to 80 °C in oil bath. Then the initiator solution and the rest of the monomer solution were separately fed into the vessel dropwise over 2.5 and 2.0 h respectively. The inside temperature was kept constant at 80 ± 2 °C during polymerization. After complete dosing, the whole reactant mixture was kept at 80 °C for additional post-polymerization time of 30 min under

stirring to complete polymerization and then was allowed to cool down to room temperature of 25 °C. The obtained products appeared yellowish transparent solutions with solid contents in a range of 36.0–38.0 wt%.

2.1.6 Antifoaming Agent

RHODOLINE DF 642, antifoaming agent, was provided by Rhodia (China) Co. Ltd.

2.1.7 Sand

Both standard sand (complying with GB178) and 40–70 mesh quartz sand were used for the preparation of mortar specimens.

2.1.8 Deionized Water

Deionized water was used in all experiments in this research including the synthesis of polymers and the preparation of cement pastes and mortars.

2.2 Characterization of the Synthesized Polymers

2.2.1 Size Exclusion Chromatography (SEC)

SEC has been a standard method for polymer fractionation and analysis of molecular weight distribution of polymers based on separation of polymer fractions with different molecular size, i.e. hydrodynamic volume. Integration of a light scattering instrument in the SEC system allows obtaining absolute molecular weights that do not rely on calibration with standards of known molecular mass. In this research, SEC equipped with a multi-angle laser light scattering (LS) detector (DAWN HELEOS II, Wyatt Technology, USA) and a refractive index (RI) detector (Optilab rEX, Wyatt Technology, USA) was used to determine the Mw, number average molecular weight (Mn) and the polydispersity (PDI) of the prepared polymers. Meanwhile, polymer content in the prepared polymer solution can be estimated by separation of polymers and oligomers with relatively high molecular weight from the synthesized product, which contains polymers, oligomers, macro-monomers (Mw of ca. 1300) and probably residual monomers with lower

molecular weight than 1000. For all polymers, 0.1 mol/L NaNO_3 solution at pH of 7 was used as the eluent in SEC measurement. The synthesized polymers were diluted to concentration of 5 mg/mL (10 mg/L for samples of PAM0-100, PAS0-100, PMAPTAC) and directly injected into a 0.2 mL loop with a spectra system auto sampler. Temperature during measurement was kept constant at 25 °C and the flow rate was adjusted to 0.5 mL/min. SEC columns of SB-804 HQ connected with SB-802.5 HQ (OHpak, Shodex, USA) were used for SEC measurement of all polymers.

2.2.2 Purification of the Synthesized Polymers

As well understood that the synthesis of co-polymers cannot reach conversion of 100% and known from the result of SEC measurements, the obtained samples from the synthesis of the co-polymers contain fractions of polymers, oligomers, un-reacted macro-monomer and those monomers with smaller molecular weight, and a tiny amount of salts from decomposition of initiator. In this research, dialysis technique was adopted to remove un-reacted monomers, salts and a part of oligomers with small molecular weights from the samples and to obtain purified co-polymer solutions, as shown in Fig. 2.4. A cellulose ester semipermeable membrane MD44-7 with nominal molecular weight cut-off of 7000 Da provided by Beijing Ruida Henghui Science and Technology Development Co. Ltd was used, which allows globulin with molecular weight of 7000 and smaller molecules to pass through. The synthesized product was firstly diluted to 10.0 wt% and then 40 mL of the diluted polymer solution was introduced into a dialysis bag with diameter of 25 mm and length of 300 mm, which is made of the semipermeable membrane.

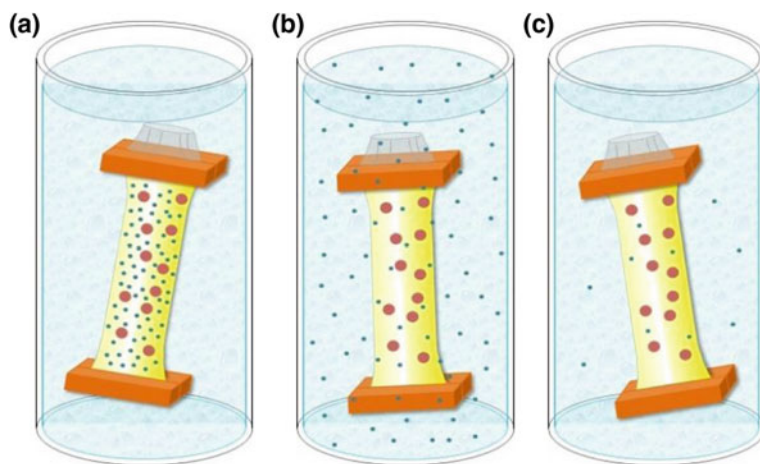
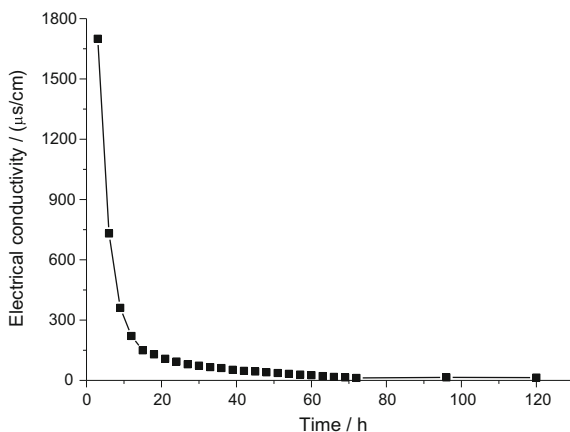


Fig. 2.4 Purification of the synthesized polymers

Fig. 2.5 Development of electrical conductivity of the dialysate during dialysis of the synthesized samples



Subsequently, 10 completely sealed dialysis bags filled with the polymer solutions were placed into a container filled with 5000 mL deionized water as dialysate. In order to accelerate the diffusion process of the monomers and salts across the semipermeable membrane, the water bath was kept at 40 °C under stirring and renewed every 3 h. The electrical conductivity of the dialysate was measured by using a conductivity meter (FE30, Mettler Toledo, Switzerland) every 3 h before the dialysate was renewed. It is noticed from Fig. 2.5 that the electrical conductivity of the dialysate sharply decreased at the beginning of the dialysis (first 24 h), which indicated a fast diffusion of the salts and monomers from the sample inside the dialysis bag to the water bath. With continuous dialysis for 4 days, the electrical conductivity of dialysate kept slowly decreasing. Knowing that the electrical conductivity of deionized water was about 10 $\mu\text{S}/\text{cm}$, we ended the dialysis process when the electrical conductivity of dialysate dropped below 30 $\mu\text{S}/\text{cm}$. Thus, most of salts, residual monomers and oligomers that are able to pass across the semipermeable membrane were effectively removed from the sample. After purification by dialysis, the solid content of the obtained solution was measured. From this value, information about the polymer content in the original synthesized product can be calculated. In this manner, the synthesized products, including PMAPTAC homo-polymer, PAM and PAS co-polymers were purified for Fourier transform infrared spectrum (FTIR) analysis and for all the following investigations on their behaviors in cementitious system.

2.2.3 Fourier Transform Infrared Spectrum (FTIR)

The chemical structures of the purified co-polymers were characterized by FTIR (Nicolet 6700 FTIR, Thermo Fisher Scientific, USA) instrument with a resolution of 4 cm^{-1} . The purified co-polymer solution was homogeneously mixed with KBr

salt and completely dried in a vacuum oven at 80 °C. The mixture was pressed into a tablet and then scanned in the transmission mode from 400 to 4000 cm^{-1} at room temperature of 25 °C.

2.3 Specimens Preparation

2.3.1 *Fresh Cement Pastes with the Three Types of Chemical Admixtures*

Fresh cement pastes (FCPs) with different W/Cs and varied dosages of superplasticizers, latexes and asphalt emulsions at different temperatures were prepared, which respectively correspond to the Cement-Superplasticizer-Water system, Cement-Latex-Water system and Cement-Asphalt-Water system according to the admixture contained in the FCPs. The formulations of the FCPs are shown in Table 2.5. P/C is defined as the mass solid/solid ratio of polymer to cement. Sp/C, L/C and A/C respectively refer to the mass solid/solid ratios of superplasticizer to cement, latex to cement and asphalt emulsion to cement. W/C is the water to cement ratio. The amount of water in the chemical admixtures was incorporated into the calculation of W/C ratio. A/P denotes the antifoaming agent to polymer ratio in all specimens. Cement I was adopted in the preparation of Cement-Superplasticizer-Water system and Cement-Latex-Water system while Cement III was used in the Cement-Asphalt-Water system.

Before preparing the FCPs, all the raw materials and the mixing bowl as well as the mixer rotor were stored in an environmental chamber with temperature of 0, 20 and 40 °C for 24 h. Then, the raw materials were mixed in accordance with the Chinese standard GB/T8077 and the detailed mixing procedure is described as follows. (1) Water, chemical admixtures and antifoaming agent were firstly added into a mixer and mixed well. (2) Cement was gradually introduced over a time span of 2 min into the mixer at 62 rpm. After a 10 s interval, mixing was resumed for an additional 2 min at 125 rpm. The whole mixing process took about 5 min in total. (3) After being mixed, the freshly mixed paste was kept in a mixing bowl covered with a soaked towel to avoid water evaporation and was then stored at constant environmental temperatures equal to the targeted test temperatures for 0, 25, 55, 85 and 115 min. Thus, counting from the time point of water-cement contact, each paste was actually tested at 5, 30, 60, 90 and 120 min after the contact of cement with water.

Table 2.5 Formulations of fresh cement pastes

Chemical admixtures	P/C ^a (%)	W/C	A/P	0 °C	20 °C	40 °C
PCE superplasticizer	0.00	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.05	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.10	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.15	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.20	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.30	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.40	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.50	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.60	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.70	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.80	0.25, 0.29, 0.35, 0.4	0	√	√	√
	0.90	0.25, 0.29, 0.35, 0.4	0		√	
	1.00	0.25, 0.29, 0.35, 0.4	0		√	
	1.50	0.25, 0.29, 0.35, 0.4	0		√	
	2.00	0.25, 0.29, 0.35, 0.4	0		√	
	0.00	0.14, 0.15, 0.2, 0.33	0		√	
	0.10	0.14, 0.15, 0.2, 0.33	0		√	
	0.20	0.14, 0.15, 0.2, 0.33	0		√	
	0.30	0.14, 0.15, 0.2, 0.33	0		√	
	0.40	0.14, 0.15, 0.2, 0.33	0		√	
	0.50	0.14, 0.15, 0.2, 0.33	0		√	
	0.60	0.14, 0.15, 0.2, 0.33	0		√	
	0.70	0.14, 0.15, 0.2, 0.33	0		√	
	0.80	0.14, 0.15, 0.2, 0.33	0		√	
	0.90	0.14, 0.15, 0.2, 0.33	0		√	
	1.00	0.14, 0.15, 0.2, 0.33	0		√	
	1.50	0.14, 0.15, 0.2, 0.33	0		√	
	2.00	0.14, 0.15, 0.2, 0.33	0		√	
	0.00	0.5	0	√	√	√
	0.05	0.5	0		√	
	0.10	0.5	0		√	
	0.15	0.5	0		√	
	0.20	0.5	0		√	
	0.30	0.5	0		√	
	0.40	0.5	0		√	
	0.50	0.5	0		√	
	0.00	0.6	0	√	√	√
	0.00	0.7	0	√	√	√
	0.00	0.8	0	√	√	√

(continued)

Table 2.5 (continued)

Chemical admixtures	P/C ^a (%)	W/C	A/P	0 °C	20 °C	40 °C
	0.00	1.0	0		√	
	0.00	1.4	0		√	
	0.00	1.6	0		√	
	0.00	2.0	0		√	
	0.00	3.0	0		√	
NSF superplasticizer	0.1	0.29, 0.4	0		√	
	0.3	0.29, 0.4	0		√	
	0.5	0.29, 0.4	0		√	
	0.8	0.29, 0.4	0		√	
	1.0	0.29, 0.4	0		√	
Polymer latexes L1 and L2	0	0.5	0.02%	√	√	√
	1	0.5	0.02%	√	√	√
	3	0.5	0.02%	√	√	√
	6	0.5	0.02%	√	√	√
	9	0.5	0.02%	√	√	√
	12	0.5	0.02%	√	√	√
	20	0.5	0.02%		√	
	35	0.5	0.02%		√	
	60	0.5	0.02%		√	
Anionic asphalt emulsion	0	0.4	0.02%	√	√	√
	1	0.4	0.02%		√	
	3	0.4	0.02%		√	
	6	0.4	0.02%		√	
	9	0.4	0.02%		√	
	10	0.4	0.02%	√	√	√
	20	0.4	0.02%		√	
	35	0.4	0.02%	√	√	√
	50	0.4	0.02%	√	√	√
Cationic asphalt emulsion	60	0.4	0.02%		√	
	10	0.4	0.02%	√	√	√
	20	0.4	0.02%		√	
	35	0.4	0.02%	√	√	√
	50	0.4	0.02%	√	√	√
	60	0.4	0.02%		√	

^aMass solid/solid ratios of superplasticizer to cement, latex to cement and asphalt emulsion to cement are respectively denoted as Sp/C, L/C and A/C

Table 2.6 Initially added amount of monomers and their homo-polymers in the pastes

Item	AA	SSS	MAPTAC	PAA	PSSS	PMAPTAC	MPEGMA
(g/g cement) (%)	0.12	0.34	0.36	0.12	0.34	0.36	2.15
($\mu\text{mol/g}$ cement)	16.5	16.5	16.5	16.5	16.5	16.5	16.5

2.3.2 *Fresh Cement Pastes with the Organic Monomers and the Polymers*

To investigate the effects of $-\text{COO}^-$, $-\text{SO}_3^-$ and $\equiv\text{N}^+$ on the adsorption and cement hydration, FCPs containing the organic monomers AA, SSS, MAPTAC and the corresponding homo-polymers were prepared at the temperature of 20 °C. Cement I was used. The W/C of the pastes was set to 0.4 and the addition of the monomers and polymers was 16.5 $\mu\text{mol/g}$ cement with identical molar quantity of the functional groups. The quantity of the monomers was counted by mole of the substance and the quantity of the homo-polymers was measured by mole of the repeating units. Their mass ratios to cement are listed in Table 2.6. The same mixing procedure described in Sect. 2.3.1 was applied.

Similarly, FCPs containing the purified comb-shaped co-polymers were prepared at the temperature of 20 °C. Cement II was used and the W/C of the pastes was set to 0.35. The addition of the purified co-polymers in cement pastes was varied as 0.1, 0.2 and 0.4% by weight of cement (bwoc), respectively. The same mixing procedure described in Sect. 2.3.1 was applied.

2.3.3 *Hardened Cement Pastes and Mortars with the Three Types of Chemical Admixtures*

Cement pastes and mortars were prepared according to the formulations presented in Table 2.7. P/C is defined as the mass solid/solid ratio of polymer to cement. W/C is the water to cement ratio. Sp/C, L/C and A/C respectively refer to the mass solid/solid ratios of superplasticizer to cement, latex to cement and asphalt emulsion to cement. In the formulations of cement mortars, the mass ratio of sand to the sum of cement and polymer is expressed as S/(C + P). The antifoaming agent to polymer ratio in all specimens was set at 0.0005. All specimens were prepared in a mixer equipped with paddles rotating helicoidally at successive speeds. The mixing procedure of cement pastes and mortars followed the Chinese standards GB/T8077 and GB/T17671-1999, respectively. Three different curing conditions were used: the standard curing condition [moist curing at 20 °C and 95% relative humidity (R.H.)], the dry curing condition (1-day moist curing and 27-day curing at 20 °C and 65% R. H.) and the mix curing condition (21-day moist curing and 7-day dry curing).

Table 2.7 Mix proportions of hardened cement pastes and mortars

Polymers	Specimen no.	W/C	P/C ^a (%)	S/(C + P)	A/P (%)
PCE superplasticizer	PC-1-1-(S1)-B	0.29	0	1.33	0.05
	PC-1-2-(S1)-B	0.29	0.1	1.33	0.05
	PC-1-3-(S1)-B	0.29	0.3	1.33	0.05
	PC-1-4-(S1)-B	0.29	0.5	1.33	0.05
	PC-2-1-(S1)-B	0.29	0	1.33	0.05
	PC-2-2-(S1)-B	0.29	0.1	1.33	0.05
	PC-2-3-(S1)-B	0.29	0.3	1.33	0.05
	PC-2-4-(S1)-B	0.29	0.5	1.33	0.05
Polymer latexes	L1-1-(S1)-M	0.50	0	3.00	0.05
	L1-2-(S1)-M	0.50	1	3.00	0.05
	L1-3-(S1)-M	0.50	3	3.00	0.05
	L1-4-(S1)-M	0.50	6	3.00	0.05
	L1-5-(S1)-M	0.50	12	3.00	0.05
	L2-1-(S1)-M	0.50	0	3.00	0.05
	L2-2-(S1)-M	0.50	1	3.00	0.05
	L2-3-(S1)-M	0.50	3	3.00	0.05
	L2-4-(S1)-M	0.50	6	3.00	0.05
	L2-5-(S1)-M	0.50	12	3.00	0.05
Asphalt emulsions	AAE-1-(S2)-G	0.50	0	3.00	0.05
	AAE-2-(S2)-G	0.50	20	3.00	0.05
	AAE-3-(S2)-G	0.50	40	3.00	0.05
	AAE-4-(S2)-G	0.50	60	3.00	0.05
	AAE-5-(S2)-G	0.72	80	3.00	0.05
	CAE-1-(S2)-G	0.50	0	3.00	0.05
	CAE-2-(S2)-G	0.50	20	3.00	0.05
	CAE-3-(S2)-G	0.50	40	3.00	0.05
	CAE-4-(S2)-G	0.50	60	3.00	0.05
	CAE-5-(S2)-G	0.72	80	3.00	0.05

PC-series, L1-series, L2-series, AAE-series and CAE-series refer to the specimens with PCE superplasticizer, latex L1, latex L2, anionic asphalt emulsion and cationic asphalt emulsion respectively; S1 and S2 represent the standard sand and quartz sand, respectively; B-series, M-series and G-series respectively refer to the specimens cured under standard curing, mix curing and dry curing conditions

^aMass solid/solid ratios of superplasticizer to cement, latex to cement and asphalt emulsion to cement are respectively denoted as Sp/C, L/C and A/C

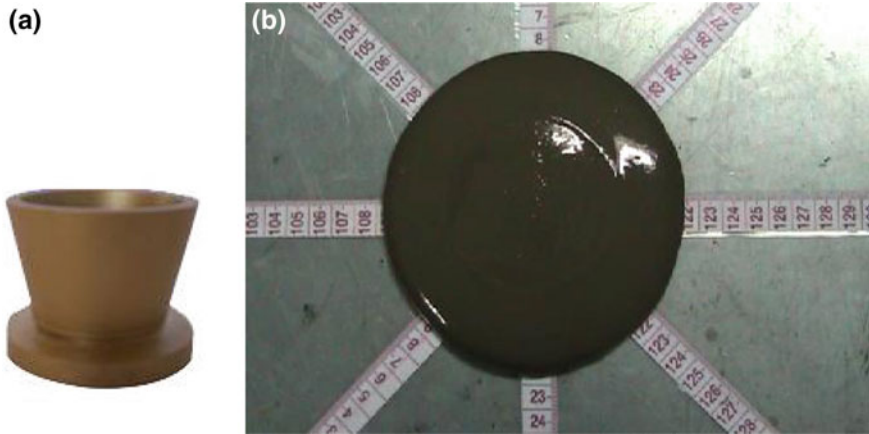


Fig. 2.6 Mini-cone test method: **a** cone and **b** spread diameter

2.4 Testing Methods

2.4.1 Fluidity Measurement

Mini-cone test is a simple and effective method to get a rough view on the fluidity of cementitious materials, which is represented by spread diameter as shown in Fig. 2.6. The spread diameter has been proved to be able to classify different materials in terms of their ability to fill a formwork. A larger spread diameter indicates superior fluidity of the pastes.

In this research, a copper cone with top diameter of 36 mm, bottom diameter of 60 mm and height of 60 mm was used (Fig. 2.6a). Before testing, all the instruments (the cone and glass plate) were stored at the targeted temperature of 0, 20 and 40 °C. The measurement was performed at 5, 30, 60, 90 and 120 min after the contact of cement with water. At every predetermined interval, a portion of the FCP was extracted and remixed at a speed of 125 rpm for 30 s to ensure the homogeneity. After that, the fresh paste was poured into the cone right away and then, the cone was quickly lifted up. After the paste stopped flowing, the average value of four perpendicularly crossing spread diameters of the cement paste was recorded. The fluidity tested at 5 min was defined as the initial fluidity and the spread diameters tested at different measuring time were defined as D_5 , D_{30} , D_{60} , D_{90} and D_{120} respectively. The whole measuring process lasted for less than 2 min and the portion of the tested FCP was abandoned as waste disposal after each test to ensure the temperature of the remaining paste unaffected.

2.4.2 Rheological Properties

The rheological properties of FCPs can be roughly described by Bingham model, in which two intrinsic rheological parameters, yield stress τ_0 and plastic viscosity μ_p are involved (Aiad 2003; Axelsson and Gustafson 2006; Roussel et al. 2007; Wallevik 2006). In this research, the two rheological parameters at different temperatures were tested by using a rheometer (Brookfield RV-III, USA). The preparing method, storing time and the measuring temperatures of the FCPs are consistent with those described in Sect. 2.4.1. The yield stress and plastic viscosity values tested at 5 min were defined as initial ones while the ones at measuring time (t) were defined as $\tau_0(t)$ and $\mu_p(t)$.

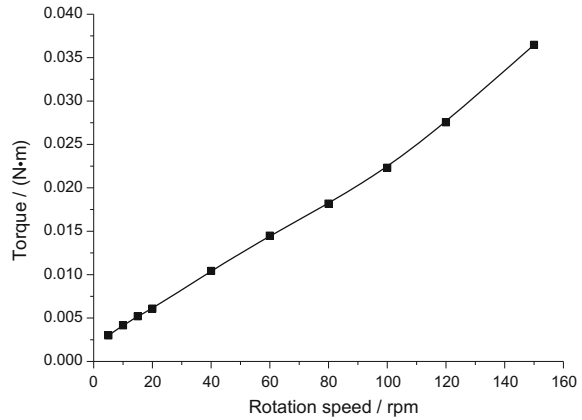
Four-bladed vane spindle V-71, V-72 and V-73 with different measuring ranges were applied during the measurement of yield stress to accommodate the varied yield stress for all the pastes, as shown Fig. 2.7b. The yield stress was measured along a cylindrical surface defined by the outer tips of the vane blades, which effectively eliminated slippage phenomenon. Before testing, the fresh paste was well mixed with a rotator mixer at a rotation speed of 125 rpm for 30 s to break the particle agglomerates in the suspension. After a pause of 10 s, a stress-strain curve of the fresh cement paste under shear stress was recorded at a rotation speed of 2 rpm by the rheometer. Yield stress was finally obtained when the fresh paste started to yield.

Regarding the measurement of plastic viscosity, standard disc spindle RV2 and RV3 were applied for the FCPs with low viscosity whilst RV4 and RV5 were used for the measurements of high viscosity paste. The same procedure of pre-shearing was performed on the FCPs before testing. Plastic viscosity of the FCPs was measured at different rotation speeds, which involved a stepwise ramp up from 5 to 150 rpm (5, 10, 15, 20, 40, 60, ..., 150 rpm). At each rotation speed, viscosity was recorded after the equilibrium was reached. Take the torque-rotation speed curve presented in Fig. 2.8 as an illustrative example, and it is seen that the FCP fairly behaves like a Bingham fluid, whose viscosity keeps almost constant after yield with the change of shear rate. As the disc spindles were used for measuring viscosity, the slippage was inevitable due to the formation of water film between the



Fig. 2.7 Brookfield RV-III rheometer (a), vane spindles (b) and disc spindles (c)

Fig. 2.8 Plot of torque versus rotation speed for the cement paste (W/C: 0.35, P/C: 0.5%, 5 min, 0 °C)



cement paste and the rotating spindle. However, if the slippage effect was strong, the slope of the curve of torque vs. rotation speed will noticeably decrease with the increase in rotation speed. This was not the case in our measurements as seen in Fig. 2.8. This suggests that the slippage effect induced by disc spindles in our tests was thought to be negligible in the testing rotation range. In this research, the viscosity at rotation speed of 100 rpm was chosen as the representative plastic viscosity.

2.4.3 Viscoelastic Properties

Fresh cement paste is considered as a viscoelastic material, because it responds to external forces in a manner intermediately between an elastic solid and a viscous fluid. Viscoelastic properties play important roles in affecting the fluidity, consistence and workability of FCPs (Bellotto 2013; Ferrandis and Leveque 2003; Grasley and Lange 2007; Nachbaur et al. 2001; Subramaniam et al. 2005; Subramaniam and Wang 2010; Wang et al. 2010).

In this research, a microrheology analyzer (Rheolaser LAB6™) was adapted to in situ follow the development of the viscoelastic properties of FCPs in the presence of PCE superplasticizer during the early hours after mixing, as presented in Fig. 2.9. This method measures the mean square displacement (MSD) of cement grains based on diffusing wave spectroscopy (DWS) and gives an insight into the elastic and viscous properties of the suspension system from a microstructural point of view. Before tests, the analyzer was equilibrated at 20 °C for 30 min. After that, the well mixed FCP was poured into a cylindrical glass cell of 20 mL with a 25 mm diameter and then placed into the channels. A fixed coherent laser beam (wavelength 658 nm) is incident upon the sample which contains scatterers (cement grains here). The MSD curves of cement grains in the FCP were continuously recorded at a constant temperature of 20 °C for 4 h. From the curves, seven



Fig. 2.9 Microrheology analyzer (Rheolaser LAB6™)

parameters including elastic index (EI), macroscopic viscosity index (MVI), storage modulus G' , loss modulus G'' , and Maxwell parameters, the viscosity of dashpot η and the elastic modulus of spring G , were extracted to quantitatively analyze the viscoelastic properties of FCPs.

2.4.4 Microstructure Examination

The rheological properties of FCPs are primarily determined by the microstructure of the paste (Barnes and Hutton 1989; Xu 1989). The observation for FCPs at a mesoscopic scale is one of the most direct way to analyze the microstructure of the FCPs and further understand the variations of the rheological properties.

2.4.4.1 Optical Microscope

A high sensitivity and high resolution analytical tool Morphologi G3 (Malvern Instruments Limited, Malvern, UK) was employed to characterize the structural organization of cement grains in different dispersion media like air, deionized water, ethanol and an aqueous solution of ethanol, superplasticizer solutions, latexes, asphalt emulsions, as shown in Fig. 2.10. The instrument captures the image of each particle by scanning the sample underneath the microscope optics, while keeping the particles in focus. Advanced graphing and data classification

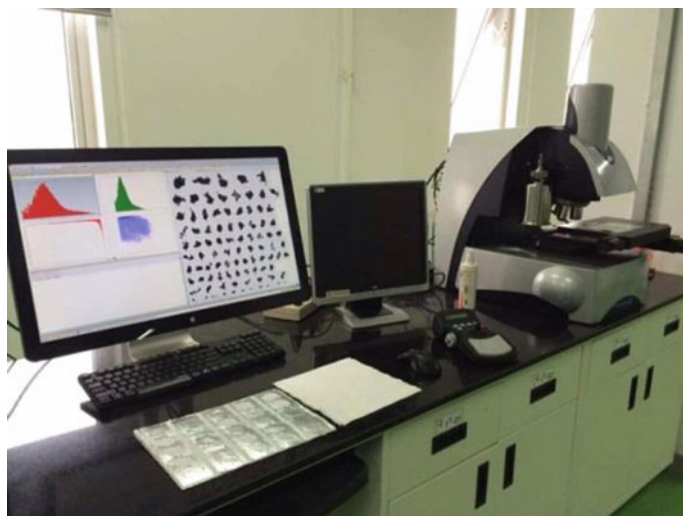


Fig. 2.10 Morphologi G3 optical microscope

options in the software ensure that the extracted relevant data concerning the morphological properties for each particle from the measurement are as straightforward as possible, via an intuitive visual interface.

The cement suspension samples with different dispersion media were prepared as follows.

- (1) C-A system: a small amount of cement powder was dispersed on a stage using an integrated dry powder disperser with an air pressure of 200 and 500 kPa.
- (2) C-E system or C-W system: cement powder was introduced into deionized water or ethanol with the mass ratio of 1:200, and then was mixed at a speed of 125 rpm for 2 min. After a 10 s interval, mixing was resumed for an additional 2 min at 125 rpm.
- (3) C-EW system: an aqueous solution of ethanol was prepared with mass ratio of ethanol to water of 1:1 and then cement powder was introduced into the solution with mass ratio of 1:200. They were mixed according to the above procedure.
- (4) C-E + C-W system: equal mass of C-E mixture and C-W mixture were taken and mixed well.
- (5) C-W-P system: three aqueous solutions with PCE mass concentration of 0.1, 0.3 and 0.5% were prepared, and then cement powder was introduced to the solutions with mass ratio of 1:200 and mixed well, respectively corresponding to C-W-P0.1, C-W-P0.3 and C-W-P0.5 system.
- (6) C-W-N0.5 system: an aqueous solution with NSF mass concentration of 0.5% was prepared, and then cement powder was introduced to it with mass ratio of 1:200 and mixed well.

- (7) C-W-L system: two aqueous solutions with latex mass concentration of 3% were prepared, and then cement powder was introduced to the solutions with mass ratio of 1:200 and mixed well.
- (8) C-W-A system: an aqueous solution with anionic asphalt mass concentration of 10% was prepared, and then cement powder was introduced to the solutions with mass ratio of 1:200 and mixed well.

The well-mixed cement suspension of 2 mL was taken and injected into a wet cell. The dispersed cement powder on the stage as well as the suspension in the wet cell were instantly subjected to the observation by Morphologi G3. In the meantime of scanning the particles, the high-quality image of each particle was captured and a 2-dimensional projection using geometrical calculations was performed on these collected images. Finally, apart from a global picture containing all the scanned particles, some structural parameters such as particle size, shape and so on, were constructed on the basis of tens to hundreds of thousands of particles. The whole process including sample preparation and analysis by Morphologi G3 lasted for 15 min. That is to say, the effects of cement hydration within such a short period can be neglected in the case of cement and water mixtures.

Moreover, a phase contrast microscope (OLYMPUS BH-2) was employed to observe the microstructure evolution of C-W-A system during the early stage of cement hydration. To clearly observe the cement grains and asphalt particles, the fresh cement paste with 20% asphalt at W/C of 0.5 was diluted 10 times to ensure that the particles in the suspension were well dispersed.

2.4.4.2 SEM

Environmental scanning electron microscope (ESEM) (FEI, Quanta 200FEG, USA) and SEM (CSM-950) were used to observe the microscopic morphology of FCPs and HCPs respectively. After well-mixing, blank FCPs, the FCPs with 0.1% PCE superplasticizer at W/C of 0.29, the FCPs with 3 and 9% latexes at W/C of 0.5, and the FCPs with 10, 35 and 60% anionic asphalt emulsion at W/C of 0.4 were observed in a low vacuum mode (300–500 Pa). Some internal parts of HCPs with 12% latexes at W/C of 0.5 cured for 28 days were taken and dried at 60 ± 2 °C for 24 h. The parts were processed by carbon-plating before being observed by SEM.

2.4.4.3 3-D Laser Scanning Microscope

In order to clearly observe the microstructure of FCPs with asphalt emulsion, a 3-D laser scanning microscope (OLYMPUS LEXT OLS4100) was employed to capture the global 2-D morphology images, 3-D morphology images and 3-D topographic maps at mass ratios of asphalt to cement of 0, 0.35, 0.6 and 1.0 and W/C of 0.4. All the observations were initiated right after the pastes were well prepared.

2.4.5 Adsorption Amount

The adsorption amounts of superplasticizers, organic monomers and polymers on cement grains were determined by total organic carbon (TOC) measurement using TOC analyzer (Shimadzu, TOC-VCPH, Japan), the measurement range of which is from 4 ppb to 4000 ppm. After well mixed, the fresh cement paste was immediately centrifuged at 3000 rpm for 10 min. A clear supernatant solution was then collected by using a membrane filter with pore diameter of 0.22 μm . Subsequently, the supernatant solution was diluted with deionized water to a suitable concentration for TOC measurement, which should be located in the range of 20–60 mg/L in order to match the 100 mg/L standard curve used in the TOC analyzer. 100 mL diluted solution was used for the measurement of concentration of carbon element. Finally, the adsorption amount on cement of per unit mass could be calculated by subtracting the amount of carbon element remaining in the aqueous solution from the amount initially added in cement paste. It should be mentioned that a tiny amount of carbon (ca. 0.014 mg/g cement) can be detected in the blank cement paste and it should be subtracted in the calculation of their adsorption amounts on cement grains. Given that the different molecular weights for AAA, SSS, MAPTAC and the corresponding homo-polymers, their adsorption amounts in cement pastes were expressed in the form of molar amount of the functional groups ($\mu\text{mol/g}$ cement) for the purpose of comparing the effects of charge properties on the adsorption behaviors. For the comb-shaped co-polymers, PCE and NSF superplasticizers, their adsorption mass on cement of per unit mass (mg/g cement) were discussed.

2.4.6 Precipitation Measurement

It has been well established that $-\text{COO}^-$ groups may chelate Ca^{2+} ions in solution (Li and Kong 2009; Pourchet et al. 2007; Yamada et al. 2000). Consequently, when AA or PAA is added into fresh cement paste, complexes, which are either water soluble or water insoluble may be formed due to the reaction between $-\text{COO}^-$ and Ca^{2+} in aqueous phase of the FCPs. If water insoluble products are formed, which are then precipitated from the solution phase, the adsorption measurement as described in Sect. 2.4.5 may give wrong results because the carbon contained in the precipitates is falsely considered as the adsorbed carbon on cement surface. Thus, the adsorption amounts of chemicals on cement surface will be overestimated. In order to confirm whether precipitates were formed when the chemicals were added into cement pastes, precipitation experiments were conducted by mixing cement pore solution with AA, SSS, MAPTAC, PAA, PSSS and PMAPTAC respectively. The measuring procedure is summarized as follows. (1) A blank cement paste with W/C of 0.4 was prepared with the same mixing procedure as described in Sect. 2.3.2. (2) After mixing for 4.25 min, a supernatant pore solution of the blank cement paste was

obtained by centrifuge in accordance with the method described in Sect. 2.4.5. (3) Subsequently, 100 mL pore solution was taken and a selected chemical was added into the pore solution. (4) According to the mixing proportions shown in Table 2.6, the dosages of AA, SSS, MAPTAC, PAA, PSSS and PMAPTAC in the pore solution of 100 mL were 0.297, 0.850, 0.908, 0.297, 0.850 and 0.908 g, respectively and the mixtures were kept stirring for 2 h. (5) The mixtures were then quietly stored for 4 h for observation of precipitation. (6) If a mixture became turbid, it was then centrifuged and filtrated to obtain the supernatant solution. (7) The concentration of the remaining chemical in solution was measured again by TOC analyzer as described in Sect. 2.4.5. This way, the precipitation ratio R of the chemical could be calculated by the formula: $R = (1 - C_1/C_2) \times 100\%$, where C_1 is the concentration of carbon element remaining in the supernatant solution after centrifuge separation and C_2 stands for the initial concentration of carbon element when the chemical was added in the pore solution. (8) By deduction of the amount of the precipitated chemical from the amount of the adsorbed chemical that was measured in Sect. 2.4.5, the overestimated adsorption amount could be corrected.

2.4.7 Particle Size and Zeta Potential

To recognize the changes in the microstructure of FCPs caused by adding PCE and NSF superplasticizers, particle size distribution and zeta potential of the cement pastes at different Sp/Cs were measured by using an acoustic and electroacoustic spectrometer (Dispersion Technology, DT 1201, USA). The measuring range of zeta potential is from -3000 to $+3000$ mV and the measuring error is in the vicinity of ± 2 mV.

The FCP was poured into a sample chamber right after mixing and was subjected to the measurement of particle size. Raw data of ultrasound attenuation within a frequency range of 3–35 MHz reflecting the microstructure of sample could provide direct information on the particle size distribution of the FCPs. Prior to measuring zeta potential, a zeta probe was calibrated by using the pore solution of cement paste as ionic background for the zeta potential measurement of the corresponding cement paste. After a mixing time of 4 min, 40 mL fresh paste was immediately transferred into a 50 mL sample cell equipped in DT1201. Afterwards, the probe was dipped into the well mixed FCP and the zeta potential was measured. The value of zeta potential was calculated from the colloidal vibration current which was determined by the measurement. During the measurement, the FCP was kept stirring by using a magnetic mixer at 200 rpm in order to keep the mixture homogeneous. The measurement of zeta potential was repeated 7 times over 10 min for each sample and an average of these zeta values was recorded.

Similarly, the effects of the organic monomers and their corresponding homo-polymers as well as the comb-shaped co-polymers on the zeta potential of FCPs were also investigated. Because of the poor fluidity of FCPs containing organic

monomers at W/C of 0.4, some of which showed spread diameters as small as 60 nm, the W/C in all the cement pastes with these chemicals was heightened to 0.5 in order to ensure the operability and the accuracy of the zeta potential measurement.

2.4.8 Cement Hydration

Heat evolution during cement hydration was monitored to reveal the influences of different chemical admixtures, organic monomers and polymers on the hydration dynamics. Two types of calorimeter were used in this research.

2.4.8.1 Iso-Thermal Calorimetry

Isothermal calorimetry was adopted to monitor the heat evolution during cement hydration at 0, 20 and 40 °C by using a TAM-air micro-calorimeter (Thermometric AB, Sweden). Before tests, the calorimeter was regulated at targeted temperatures and then equilibrated for 24 h. Thereafter, the freshly mixed pastes were promptly decanted to an ampoule of 20 mL and then placed into the channels. The heat evolution of cement hydration at the targeted temperature was recorded after an auto-equilibrium of 45 min. With respect to the heat evolution within 45 min, a syringe method was used where a 20 mL ampoule and a lid with two syringes, a stirrer and a motor were equipped. A power supply was enclosed. According to the mix proportion, cement powder and liquid were respectively placed into an ampoule cup and the syringes. Then, the ampoule was covered by the lid and placed into the channels. Subsequently, the calorimeter with the ampoule in the channel was regulated at targeted temperatures and then equilibrated for 24 h. Afterwards, the liquid was promptly injected into the ampoule and the cement powder with the liquid were mixed using the stirrer for 1 min. The heat evolution was recorded since the contact of cement with water and the record lasted for 2 h.

2.4.8.2 Semi-adiabatic Temperature Test

A self-regulated semi-adiabatic calorimeter was employed to measure the internal temperature of the paste that was kept in a well-insulated cabinet. The environmental temperature was kept constant during the entire testing period. Because of the exothermic feature of cement hydration, monitoring temperature development was a useful method for obtaining information on the hydration kinetics of cement (Li and Kong 2009; Zhang et al. 2012). The insulating cabinet was pre-calibrated to obtain its heat loss coefficient. Heat of hydration Q , expressed in joules per gram of cement (J/g), can be obtained by adding up lost heat flux over time Q_{los} and heat Q_{tc} used for changing the paste temperature. The isolated cell heat loss coefficient α_{hl} , the mixture composition and thermal capacity of each component are necessary for

calculating the Q_{los} and Q_{tc} . The hydration heat can be calculated by the following formula,

$$dQ = dQ_{los} + dQ_{tc} = \frac{\alpha_{hl}(T_t - T_{en})dt}{m_c} + \frac{m_i c_i dT}{m_c} \quad (2.1)$$

where m_i is the mass of each component of the paste (g), m_c is the mass of the cement (g), c_i denotes the thermal capacity of each component of the paste (J/(g K)), T_t represents the internal temperature of the FCP at moment t , and T_{en} is the target environmental temperature.

$$\begin{aligned} Q &= \int_0^t dQ = \frac{\alpha_{hl}}{m_c} \int_0^t (T_t - T_{en})dt + \frac{m_i c_i}{m_c} \int_0^t dT \\ &= \frac{\alpha_{hl}}{m_c} \int_0^t (T_t - T_{en})dt + \frac{m_i c_i}{m_c} (T_t - T_0) \end{aligned} \quad (2.2)$$

where T_0 is the inner temperature of the FCP at the initial moment. As mentioned above, the raw materials and samples were kept at the target environmental temperatures; thus, T_0 is equal to T_{en} . Equation (2.2) can then be rewritten as

$$Q = \frac{1}{m_c} \left\{ \alpha_{hl} \int_0^t (T_t - T_{en})dt + m_i c_i (T_t - T_{en}) \right\} \quad (2.3)$$

2.4.9 Mercury Intrusion Porosimetry (MIP)

MIP has been a standard method to determine pore structure in cementitious materials (Diamond 2000). Although it is often criticized that the pore size distribution calculated from the MIP is not the actual pore size distribution in the paste, it is still a valuable technique in making comparative assessment of the pore structure in the given system which does not require the absolute pore size (Wild 2001). Moreover, the threshold diameter and the pore volume are effective indices to reflect the variations of the connectivity and the capacity of the pore in cement pastes (Diamond 2000). Therefore, in this research, the shifts of pore size distribution, the threshold diameter and the total pore volume were respectively compared and discussed for the pastes at different W/Cs and P/Cs. After cured for 7 days and 28 days respectively, the HCPs were cut into small cylinders with diameter of 10 mm and thickness of 5 mm and placed into alcohol bath for 24 h. After 3 days storage in an oven with an ambient temperature of 60 ± 2 °C, three specimens were randomly selected and subjected to MIP tests for pore structure characterization by using Hg-porosimetry (Autopore, IV 9510, USA). Differences in mercury volume can be

found by re-intruding the pastes after the first intrusion-extrusion cycle was completed (Kaufmann et al. 2009; Moro and Böhni 2002). It is considered that a part of the mercury is entrapped in the pores of certain geometric shape in HCPs which is usually called inkbottle pores (Aligizaki 2005; Willis et al. 1998). As well known, the addition of superplasticizers brings significant effects on the rheological properties of FCPs through modifying the microstructure of the FCPs. The entrapped mercury volume may indirectly provide extra information on the structure and morphology of pores in the HCPs. Therefore, two cycles of intrusion-extrusion were performed. Entrapped mercury volume and retention factor R_f were obtained as follows (Sakai et al. 2006). $R_f = V_{en}/V_1 = (V_1 - V_2) \times 100\%/V_1$, where V_{en} is the entrapped mercury volume, V_1 and V_2 are the volume of mercury intruded during the first and the second cycle respectively.

2.4.10 Alternating Current (AC) Impedance

AC impedance spectroscopy technique has been widely used to investigate the microstructure and the permeability of hardened cementitious materials based on the relationships between the parameters of AC impedance and the structure of porous cementitious systems (Cabeza et al. 2002, 2003, 2006; Gu et al. 1994; McCarter and Brousseau 1990). AC impedance concerns the application of a low-amplitude AC excitation by surface electrodes over a range of frequencies. The current response (i.e., gain and phase angle) could be measured by the impedance analyzer.

Cubic mortar specimens with size $40 \times 40 \times 40$ mm were fabricated. Similar to the chloride permeability measurement according to ASTM C1202, after being cured, all mortars were vacuum-saturated for 2 h prior to being soaked in a saturated $\text{Ca}(\text{OH})_2$ aqueous solution for 18 h. Then, the mortars were ready for the AC impedance measurements which were performed using an impedance gain/phase analyser (Agilent 4294A, Palo Alto, CA, USA) in high-frequency range from 40 kHz to 100 MHz and a potentiostat/galvanostat (PARSTAT 2263, Amtek, USA) in low-frequency range from 0.1 Hz to 100 kHz (Zhang et al. 2011).

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